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# TIN FLOTATION USING NEWLY DEVELOPED REAGENTS

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# TIN FLOTATION USING NEWLY DEVELOPED REAGENTS

by

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## ABSTRACT

Research work was carried out to develop an efficient and economic reagent regime for tin flotation.

The study included the evaluation of a new class of tin collectors marketed under the trade name "Briquest" and the investigation of complexing reagents to annihilate the detrimental effect of polyvalent cations on tin flotation process.

By using a selected Briquest collector and due to the hydrosoluble complexes formed with EDTA reagent, conditions for an excellent tin flotation were achieved.

A sample of 0.6-0.8% Sn was upgraded by this reagent regime to a concentrate of 55% Sn at a tin recovery of 85%.

The proposed reagent regime is recommended for the flotation of tin ores.

**Keywords:** Tin, flotation, Briquest reagents, EDTA used in flotation.

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# FLOTTATION D'ÉTAIN EN UTILISANT DE NOUVEAUX RÉACTIFS

par

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## RÉSUMÉ

Des travaux de recherche ont été effectués afin d'élaborer une méthode de flottation, économique et efficace, pour l'extraction de l'étain.

L'étude a porté sur l'évaluation d'une nouvelle classe de collecteurs pour l'étain, commercialisés sous le nom de Briquest, ainsi que sur l'examen de certains réactifs de précipitation pour annihiler l'effet négatif des cations polyvalents dans la flottation de l'étain.

Des conditions excellentes pour la flottation d'étain ont été établies en utilisant un certain collecteur Briquest et le réactif EDTA pour obtenir des précipités solubles avec les ions métalliques lourds.

Un concentré contenant 55% Sn et présentant une récupération en étain de 85% a été obtenu, en utilisant ces dits réactifs pour traiter un échantillon dont l'analyse en étain était 0.6-0.8%.

L'utilisation de tels réactifs est donc recommandée pour la flottation des minerais d'étain.

**Mots-clés:** La flottation d'étain, les réactifs Briquest, EDTA utilisé dans la flottation.

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# INTRODUCTION

Flotation of tin minerals has been investigated for quite some time by many researchers from universities, private laboratories and industry.

An adequate reagent regime was sought to provide a truly efficient and inexpensive tin collector and to deal with the detrimental effect of the polyvalent ions present in the pulp.

The most common tin collectors presently used are the sulfosuccinamates and styrene phosphonic acid. The former, is not very selective and the latter, although an efficient cassiterite collector is very expensive and is only soluble in caustic solutions.

It is also well known that the cassiterite flotation is very sensitive to heavy-metal ions, like $Ca^{2+}$ and especially $Fe^{3+}$ which form insoluble precipitates with the reagents, interfering thus with tin flotation.

CANMET had recognized the need to address these two major contributing factors for an efficient tin flotation and has initiated a research program to find an adequate tin collector and to annihilate the negative effect of the polyvalent cations.

The search for a suitable tin collector led to a group of organophosphonate reagents marketed by Albright and Wilson under the trademark of "Briquest". These reagents have a variety of applications among which is ore flotation. It was decided to study the possibility of finding a suitable tin collector among the members of this group of reagents.

Searching for a suitable chemical complexing agent was then initiated, to eliminate the detrimental effect of heavy-metal ions on tin flotation. By treating the flotation pulp with such a reagent, hydrosoluble complexes could be formed and the perturbing action of $Fe^{+3}$ ions could be impeded.

The research work to find an adequate reagent regime for tin flotation was carried out using an ore sample from the Rio Kemptville operation, containing approximately 0.7% Sn.

The following are the results of this research work.

## 1. OUTLINE OF THE INVESTIGATION

A research program was carried out to develop an adequate reagent regime for tin flotation using a sample of 0.6-0.8% Sn.

### 1.1 Objectives of the Investigation

The objectives of the investigation were:

a) Develop an adequate reagent regime for tin flotation using:
   - an efficient, inexpensive tin collector,
   - a suitable complexing agent for polyvalent ions.

b) Produce a saleable tin concentrate of over 50% Sn from a cassiterite ore containing 0.6-0.8% Sn.

### 1.2 Summary of the Results

An efficient reagent for tin flotation was developed using a Briquest reagent as tin collector and EDTA, as a complexing agent to annihilate the negative effect of some heavy-metal ions.

#### 1.2.1 Briquest reagents

Briquest reagents belong to a group of organophosphonates marketed by Albright and Wilson of England. The tested reagents were sodium salts of alkyl-imino-bis-methylene

phosphonic acid with chain lengths varying from n-propyl (3 carbon) to do-decyl (12 carbon). A total of 8 reagents were screened to determine their collecting properties for tin flotation.

The best results were obtained with the reagent 2N-81-25S, the sodium salt of the n-octyl imino-bis-methylene phosphonic acid. The cost of this reagent is quite low ($3-4/kg) as compared with that of SPA ($16/kg).

### 1.2.2 Complexing agents

It was proved that tin flotation results were significantly improved in the presence of EDTA (ethylene-diamine-tetra-acetic acid) a chemical complexing agent. It is believed that due to the hydrosoluble complexes formed with EDTA, the negative effect of the $Fe^{3+}$ ions was eliminated creating favourable conditions for a more efficient tin flotation. A water soluble salt of EDTA was used to facilitate the dissolution of the complexing agent.

### 1.2.3 Ore samples

Two ore samples, originating from the Rio Kemptville tin operation were used in this investigation. The main characteristics of the samples are given in Table 1.

**Table 1. Sample Characteristics**

| Sample Origin | Assay % | | % Distribution -75 $\mu$m | | Use of Sample |
|---|---|---|---|---|---|
| | Sn | S | Particles | Sn | |
| Fine Spiral Feed | 0.219 | 0.62 | 93.9 | 94.7 | Reagents' screening |
| Table Tailing | 0.63 | 1.21 | 49.5 | 86.9 | Tin flotation |

An image analysis study performed on "Table Tailing" sample indicated that approximately 90% of the cassiterite is in liberated particles. The size of those particle ranges between 4 to 20 $\mu$m.

### 1.2.4 Flotation conditions and results

The "Table Tailing" sample was used to investigate the tin flotation.

The recovery of tin minerals by flotation was achieved in two steps:

- In the first step the removal of sulphides was performed.
- In the second step a tin rougher concentrate was recovered. This concentrate was further upgraded by successive flotation cleanings.

No grinding or desliming of the ore was performed.

Sulphides removal and tin extraction was carried out in open circuit as shown in Fig. 1.

To remove the sulphides, Na-isopropyl xanthate and MIBC (methylisobutyl carbinol), at natural pH were used.

Tin flotation was carried out at pH 4, using complexing reagents (EDTA and sodium silico-fluoride), the Briquest collector and DF-250 as frother.

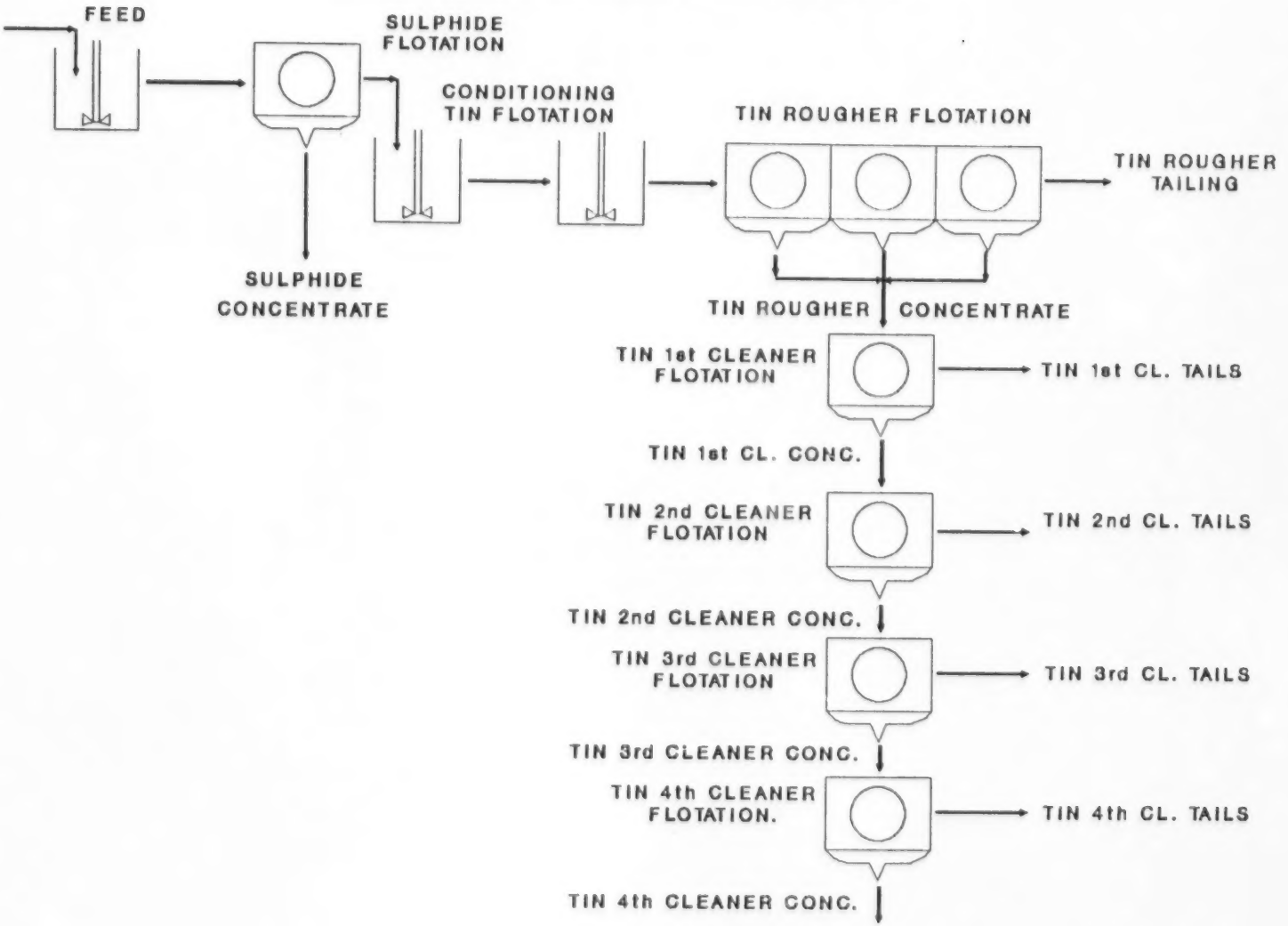
The best flotation results are given in Table 2.

**Table 2. Summary of Flotation Results**

| Product | Weight % | Assay % | | % Distribution | |
|---|---|---|---|---|---|
| | | Sn | S | Sn | S |
| Sulphides Product | 3.7 | 0.64 | 25.6 | 3.1 | 88.0 |
| Tin Final Concentrate | 1.2 | 54.9 | 0.66 | 85.2 | 0.7 |
| Middlings | 4.9 | 0.84 | 1.2 | 5.2 | 5.4 |
| Table Tailing | 90.2 | 0.056 | 0.07 | 6.5 | 5.9 |
| Head (calc.) | 100.0 | 0.77 | 1.08 | 100.0 | 100.0 |

The results indicated that the Table Tailings sample was upgraded by using this reagent regime to a concentrate of approximately 55% Sn with a tin recovery of 85%.

## Figure 1.
## Sulphides removal and tin flotation



The relationship between grade and recovery for this tin flotation is graphically shown in Fig. 2.

### 1.3 Conclusions

The following conclusions can be drawn from the results of this research work:

a) A reagent regime leading to excellent metallurgical results was developed for tin minerals flotation. The success of this flotation regime was mainly due to the following reagents:
   - Briquest, 2N-81-25S an inexpensive and very selective tin collector.
   - EDTA, a chemical complexing agent.

b) Under the best laboratory conditions a saleable concentrate of 55% Sn, for a tin recovery of 85% was obtained from an ore sample containing 0.6-0.8% Sn.

The flotation regime developed in this study can be used to recover tin from various other cassiterite ores, although some adjustments of the conditions and/or reagents addition might be required.

## 2. DESCRIPTION OF THE INVESTIGATION

### 2.1 Ore Samples

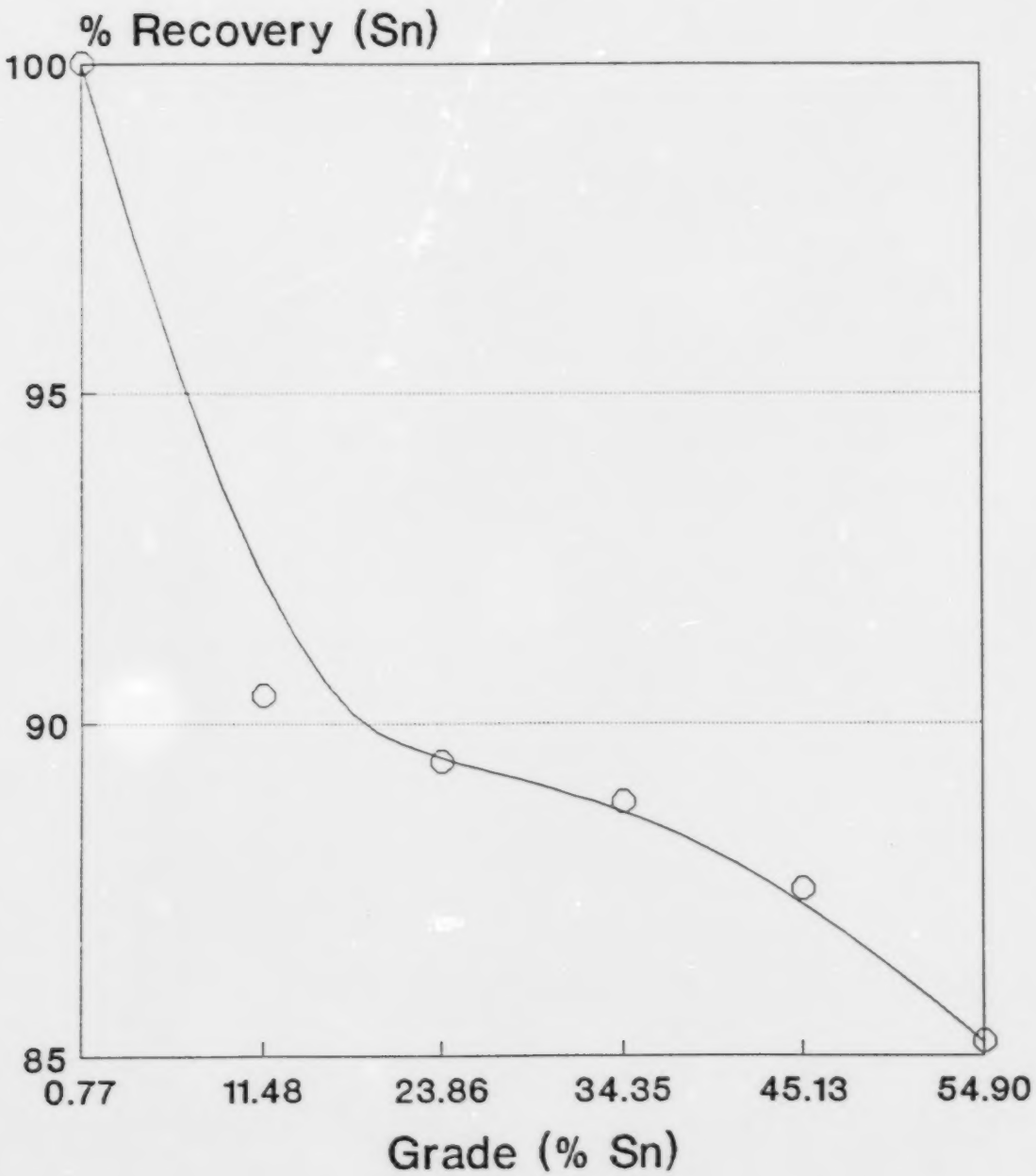
#### 2.1.1 Assay and structure

Two ore samples, both from the Rio Kemptville operation were used in this investigation.

The first sample, identified as Fine Spiral Feed was employed in the preliminary tests to screen the Briquest reagents and select the most adequate tin collector.

# Fig. 2 - Grade-Recovery Relationship

Tin Flotation



The other sample, identified as Table Tailing was used to develop the optimum conditions for tin flotation.

The chemical assay of the head samples is presented in Table 3 while the ore structures, tin and sulphur distribution on size fractions is given in Table 4.

On both samples most of the tin reported to the fine sized fractions.

**Table 3. Assay of Head Samples**

| Sample | Assay % | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Sn | S | Fe | As | Pb | Cu | Zn | Ca | Mg |
| Fine Spiral Feed | 0.219 | 0.62 | 2.12 | | <0.01 | 0.18 | 0.30 | | |
| Table Tailing | 0.63 | 1.21 | 2.02 | 0.035 | <0.01 | 0.10 | 0.35 | 0.59 | 0.03 |

### 2.1.2 Mineralogy

A mineralogical examination of the Table Tailing sample was performed to determine its mineralization and the associations of tin minerals with other species.

It was found that approximately 90% of the cassiterite is in liberated particles. The size of those particles ranges between 4 to 20 micrometers.

The sulphides, represented mainly by pyrite are also well liberated, with grains' size smaller than 55 micrometers.

The complete results of the mineralogical studies are presented in Appendix 1.

## Table 4. Size and Elements' Distribution in the Samples

| Sample | Size, Microns | Weight % | | | Assay % in retained frac. | | % Distribution in retained frac. | |
|---|---|---|---|---|---|---|---|---|
| | | Retained | | Passing, Cumul. | Sn | S | Sn | S |
| | | Individ. | Cumul. | | | | | |
| Fine Spiral Feed | +149 | 1.6 | 1.6 | 98.4 | | 0.31 | | 0.7 |
| | 105 | 1.6 | 3.2 | 96.8 | 0.153 | 0.82 | 5.3 | 2.0 |
| | 74 | 2.7 | 5.9 | 94.1 | | 0.75 | | 2.0 |
| | 53 | 5.6 | 11.5 | 88.5 | 0.124 | 0.39 | 4.0 | 3.3 |
| | 37 | 29.2 | 40.7 | 59.3 | 0.105 | 0.22 | 17.9 | 9.6 |
| | -37 | 59.3 | 100.0 | - | 0.21 | 0.93 | 72.8 | 82.4 |
| | Total | 100.0 | - | - | 0.17 | 0.67 | 100.0 | 100.0 |
| Table Tailing | +210 | 4.2 | 4.2 | 95.8 | 0.31 | 0.72 | 2.2 | 3.0 |
| | 149 | 10.2 | 14.4 | 85.6 | 0.16 | 0.42 | 2.7 | 4.2 |
| | 105 | 7.3 | 21.7 | 78.3 | 0.12 | 0.48 | 1.5 | 3.5 |
| | 74 | 28.8 | 50.5 | 49.5 | 0.14 | 0.77 | 6.7 | 22.0 |
| | 53 | 12.0 | 62.5 | 37.5 | 0.38 | 1.37 | 7.5 | 16.3 |
| | 37 | 14.8 | 77.3 | 22.7 | 0.82 | 1.03 | 20.0 | 15.2 |
| | -37 | 22.7 | 100.0 | - | 1.58 | 1.59 | 59.4 | 35.8 |
| | Total | 100.0 | - | - | 0.60 | 1.00 | 100.0 | 100.0 |

## 2.2 Briquest Reagents

Finding an efficient tin collector was certainly, the main objective of this study. Therefore, before optimizing the flotation regime for tin recovery it was considered important to find a good tin collector.

A group of reagents marketed by Albright and Wilson under the trade name "Briquest" were chosen to be investigated as potential tin collectors.

### 2.2.1 Reagents' characteristics

Briquest reagents belong to a family of organophosphonates known for uses such as scale and corrosion control, ore flotation, dispersing and stabilizing agents of various solutions.

The phosphonates are derivatives of phosphorous acid in which the hydrogen atom attached to phosphorus has been replaced by another grouping, essentially forming a compound with a C-P bond. These products are generally represented by the structure $RC(X)_2P(O)(OH)_2$ where R can be a simple or substituted alkyl/aryl group and X is hydrogen. The product is usually offered either as the free acid or a salt.

A list of some Briquest reagents is given in Table 5. The numbering system that has been adopted indicates their chemical composition and the active strength of the phosphonate in the aqueous solution. It can be seen for example that for the product 301-50A, which is an aqueous solution of nitrilotrismethylenephosphonic acid, the first digit 3 refers to the number of methylenephosphonate group present, the second digit O signifies the number of other carbon atoms and the third digit the number of nitrogen atoms. In the suffix the number 50 is the percentage of phosphonic acid in the aqueous solution as sold and the letter A indicates that product is in the acid form. The only variation to this coding is where the alkyl group of a chain aminomethylenephosphonate is either straight or branched. Straight chains are indicated by the letter N between the first and second digits. Also if the products

are sold as solutions of sodium, potassium and ammonium salts that A is replaced respectively by either S, K or N.

Most of the Briquest phosphonates are clear to pale yellow to brown aqueous solutions of the free acids or its ammonium, sodium and potassium salts which have a faint odour. Most have freezing points of 0°C or below and the solutions are miscible with water in all proportions. PH's of the solutions of the acid products are less than 2 but all salts are manufactured to a neutral pH. Densities vary between 1.18 and 1.45 depending on the strength of the solution offered and type of product.

**Table 5. Typical Properties of some Briquest Products**

| "BRIQUEST" | Compound | Acid mol. wt. | Active Matter | | Chloride | Relative Density at 20°C |
|---|---|---|---|---|---|---|
| | | | as acid % w/w | as salt % w/w | % w/w | |
| 231-25S | Na salt | 247 | 25 | 29 | 5 | 1.25 |
| 2N31-25S | Na salt | 247 | 25 | 29 | 5 | 1.25 |
| 2N41-25S | Na salt | 261 | 25 | 29 | 5 | 1.23 |
| 2N61-25S | Na salt | 289 | 25 | 29 | 5 | 1.21 |
| 2N71-25S | Na salt | 303 | 25 | 29 | 5 | 1.20 |
| 281-25S | Na salt | 317 | 25 | 28 | 5 | 1.20 |
| 2N81-25S | Na salt | 317 | 25 | 28 | 5 | 1.19 |
| 291-25S | Na salt | 331 | 25 | 28 | 5 | 1.18 |
| 2121-25S | Na salt | 373 | 25 | 28 | 7 | 1.19 |
| 301-50A | Acid | 299 | 50 | - | 0.4 | 1.34 |
| 422-100A | Acid | 436 | 97 | - | 0.2 | powder |
| 422-18N | $NH_4$ salt | 436 | 18 | 22 | 4 | 1.12 |
| 422-22K | K salt | 436 | 22 | 33 | 5 | 1.26 |

The more widely-used phosphonates, have been tested, and show remarkably low toxicity. The phosphonates are virtually non-toxic, having LD50 dosage in the range 2000 to 5000 milligrams per kilogram of body-weight. On the same basis the LD50 value for

sodium chloride is 3000 milligrams. Two of the free acids have been shown to be only mild skin irritants.

From the aspect of environmental acceptability, it has been shown that phosphonates do not interfere with the normal operation of sewage treatment processes, and that they are themselves slowly biodegraded to orthophosphate. Thus phosphonates are thought to be safe and acceptable chemicals to use. In 48-hr. tests on rainbow trout under static conditions LC50 values of 4000 - 40,000 mg/L have been found.

A useful property possessed by certain Briquest phosphonates, which contain long chain alkyl groups in the molecule, is that they have been found to reduce the surface tension of water to a similar degree found for the classical wetting agents, i.e. alkyl sulphates and sulphonates etc. These products still retain the chelating properties of their phosphonate group.

Because of their strong adsorption and surfactant properties it seems likely that phosphonates will find applications in ore flotation.

### 2.2.2 Test to select a suitable Briquest reagent

A series of tests was carried out to examine a number of Briquest reagents as potential tin collectors and to select one or more that seemed to be most appropriate for this job. The reagents to be examined were chosen from the Briquest group on the basis of their characteristics and manufacturer's information regarding their possible application. They were all sodium salts of phosphonic acid.

A tin ore sample identified as "Fine Spiral Feed" from Rio Kemptville operation was used for screening the Briquest reagents. The sample assayed 0.219% Sn and 0.62% S. Because of the relatively low sulphur content of the sample the sulphide minerals were not removed prior to tin flotation. Each Briquest reagent was tried under four pH conditions: 5,7,9 and 11.

The flotation tests to screen the Briquest reagents were carried out in an 1 litre Nagahm laboratory cell under the following conditions:

| | |
|---|---|
| Grinding: | 93.5% - 38 $\mu$m |
| pH: | variable (5-11) |
| Reagents: | $H_2SO_4$ as pH modifier (pH 5) |
| | Lime as pH modifier (pH 9 and 11) |
| | Briquest reagents as tin collector, MIBC as frother. |
| Flotation time: | Rougher flotation: 3 minutes |
| | Scavenger flotation: 2 minutes |

The results of these tests are summarized in Table 6.

The selection of a suitable tin collector was based on the tailing assay (% Sn) and tin recovery in the concentrate. When however the weight yield of the concentrate became excessively high (over 35% wt) the conditions were considered unacceptable and the reagent was eliminated.

On the basis of the results of these tests, Briquest reagent 2N-81-25S was selected to be further investigated as a potential tin collector. Using this reagent, at pH 5, the recovery of tin in the concentrate reached 76.7% for a weight yield of 24.8% and the lowest tin assay in the tailing (0.062% Sn).

## 2.3 Flotation Testwork

After the selection of an optimum Briquest reagent, a flotation research program was initiated to find the conditions under which a saleable tin concentrate at a high recovery could be produced.

Another sample, of higher tin assay (0.6-0.8% Sn) than the first one was used for this research work. The sample originating from the same tin operation (Rio Kemptville) was identified as Table Tailing.

**Table 6. Results of Tests to Select a Briquest Reagent**

| Briquest Reagent | pH | Concentrate | | | | | Tails | |
|---|---|---|---|---|---|---|---|---|
| | | % wt | Assay % | | % Recovery | | Assay % | |
| | | | Sn | S | Sn | S | Sn | S |
| 2N-31-25S | 5 | 4.4 | 0.177 | 10.53 | 3.6 | 58.7 | 0.219 | 0.34 |
| | 7 | 5.3 | 0.172 | 7.24 | 4.2 | 49.1 | 0.221 | 0.42 |
| | 9 | 5.7 | 0.163 | 7.30 | 4.2 | 48.4 | 0.224 | 0.47 |
| | 11 | 5.0 | 0.178 | 7.73 | 3.8 | 50.4 | 0.235 | 0.40 |
| 2N-41-25S | 5 | 7.4 | 0.161 | 6.66 | 5.5 | 62.5 | 0.222 | 0.32 |
| | 7 | 6.8 | 0.170 | 5.60 | 4.3 | 51.2 | 0.275 | 0.39 |
| | 9 | 6.0 | 0.175 | 6.74 | 4.7 | 50.6 | 0.224 | 0.42 |
| | 11 | 6.6 | 0.168 | 5.71 | 4.8 | 49.0 | 0.237 | 0.42 |
| 2N-61-25S | 5 | 7.7 | 0.791 | 6.35 | 26.5 | 61.6 | 0.183 | 0.33 |
| | 7 | 11.4 | 0.588 | 4.21 | 32.8 | 64.4 | 0.163 | 0.30 |
| | 9 | 9.9 | 0.264 | 4.37 | 11.7 | 56.5 | 0.219 | 0.37 |
| | 11 | 15.3 | 0.232 | 2.92 | 15.8 | 62.2 | 0.223 | 0.32 |
| 2N-71-25S | 5 | 7.4 | 0.528 | 6.39 | 18.6 | 59.3 | 0.185 | 0.35 |
| | 7 | 11.1 | 0.675 | 3.62 | 37.2 | 59.3 | 0.142 | 0.31 |
| | 9 | 10.2 | 0.400 | 4.34 | 19.3 | 51.2 | 0.190 | 0.47 |
| | 11 | 25.4 | 0.070 | 2.04 | 36.1 | 68.5 | 0.189 | 0.32 |
| 2N-81-25S | 5 | 24.8 | 0.620 | 2.33 | 76.7 | 76.9 | 0.062 | 0.23 |
| | 7 | 34.8 | 0.469 | 1.77 | 78.9 | 82.5 | 0.067 | 0.20 |
| | 9 | 25.2 | 0.523 | 2.33 | 65.7 | 73.0 | 0.092 | 0.29 |
| | 11 | 57.1 | 0.297 | 1.09 | 77.0 | 81.9 | 0.118 | 0.32 |
| 281-25S | 5 | 13.9 | 0.673 | 3.93 | 45.6 | 80.9 | 0.130 | 0.15 |
| | 7 | 25.0 | 0.562 | 2.37 | 67.5 | 80.6 | 0.090 | 0.19 |
| | 9 | 16.5 | 0.423 | 2.98 | 33.8 | 65.5 | 0.164 | 0.31 |
| | 11 | 37.0 | 0.280 | 1.50 | 46.9 | 75.3 | 0.186 | 0.29 |
| 291-25S | 5 | 34.4 | 0.441 | 1.85 | 73.8 | 80.8 | 0.082 | 0.23 |
| | 7 | 58.6 | 0.305 | 1.18 | 86.9 | 90.3 | 0.065 | 0.18 |
| | 9 | 43.0 | 0.367 | 1.42 | 73.5 | 82.4 | 0.100 | 0.23 |
| | 11 | 66.4 | 0.261 | 0.95 | 78.1 | 86.7 | 0.145 | 0.29 |
| 2121-25S | 5 | 9.6 | 0.272 | 4.46 | 12.0 | 56.1 | 0.212 | 0.37 |
| | 7 | 57.2 | 0.317 | 1.18 | 88.1 | 91.8 | 0.057 | 0.14 |
| | 9 | 59.7 | 0.308 | 1.13 | 85.0 | 91.3 | 0.081 | 0.16 |
| | 11 | 57.7 | 0.249 | 1.06 | 64.2 | 81.9 | 0.190 | 0.32 |

The testwork consisted of two parts. In the first part the sulphides removal was studied while in the second part investigation was carried out to recover the tin minerals.

These tests were performed in a Denver laboratory flotation cell. No grinding or desliming of the ore was used. Description of this work follows:

### 2.3.1 Sulphides removal

Prior to tin flotation it was necessary to remove the sulphides which otherwise would have impurified the tin concentrate.

The sulphides consisted mostly of pyrite. A typical pyrite flotation employs xanthate amyl and a frother, in an acid medium. However, in an attempt to remove as much of the sulphides minerals as possible, more detailed investigations were carried out. The additional tests included the study of pH, various activators, collectors, frothers and even a two-stage sulphides removal (pyrite and arsenopyrite flotation).

The results of all these tests are kept on file. The conclusions of the investigation can be summarized as follows:

a) <u>pH</u>

The most convenient pH for sulphides flotation was found to be 6.2-6.4 (natural). Below 6, the pH becomes favourable for cassiterite flotation and as a result some tin losses in the sulphide product can be expected.

b) <u>Activators</u>

The use of sodium sulphide or copper sulphate was found unnecessary and even harmful. Sulphides recovery was not improved and tin losses in the sulphide product increased to almost double as compared with conditions where no activator was used.

c) Collector

Two collectors were tried: xanthates 350 (K-amyl) and 343 (Na-isopropyl). It was found that the xanthate 350 was less selective for sulphide flotation and increased tin losses. Therefore the preferred collector was xanthate 343.

d) Frother

Two frothers were used: MIBC (methyl-isobutyl-carbinol) and DF-250. The preferred frother was MIBC. Dow Froth frother increased tin losses in the sulphide product.

e) Two-stage sulphides removal

Flotation of pyrite followed by arseno-pyrite removal proved to be of no benefit. The tin losses increased drastically without appreciably improving the sulphides removal.

On the basis of the results of all these flotation tests the following conditions were selected for sulphides removal:

- no grind
- pH: natural (6.2-6.4)
- Xanthate 343: 25 g/t (3 minutes)
- MIBC: 50 g/t (1 minute)
- Flotation time: 1.5-2.0 minutes

Under these conditions 85-90% of the sulphur (tied up in sulphides) contained in the ore was removed in the sulphide product. The tin loss was approximately 3%.

### 2.3.2 Tin flotation

After studying the sulphides removal, detailed research work was carried out to develop an efficient flotation regime for tin recovery.

The following conditions were investigated:

a) Complexing the heavy metal ions

Heavy metal ions present in the pulp interfere with tin flotation by forming insoluble compounds with the collectors. Sodium silicofluoride, $Na_2SiF_6$, is a complexing agent frequently used to correct this problem in tin flotation.

However, since the use of the $Na_2SiF_6$ was still not creating conditions entirely satisfactory for tin flotation, research work continued and an additional, more efficient, complexing agent was found that significantly improved the recovery of tin minerals. That was EDTA, the sodium salt of the ethylene diamine tetra acetic acid.

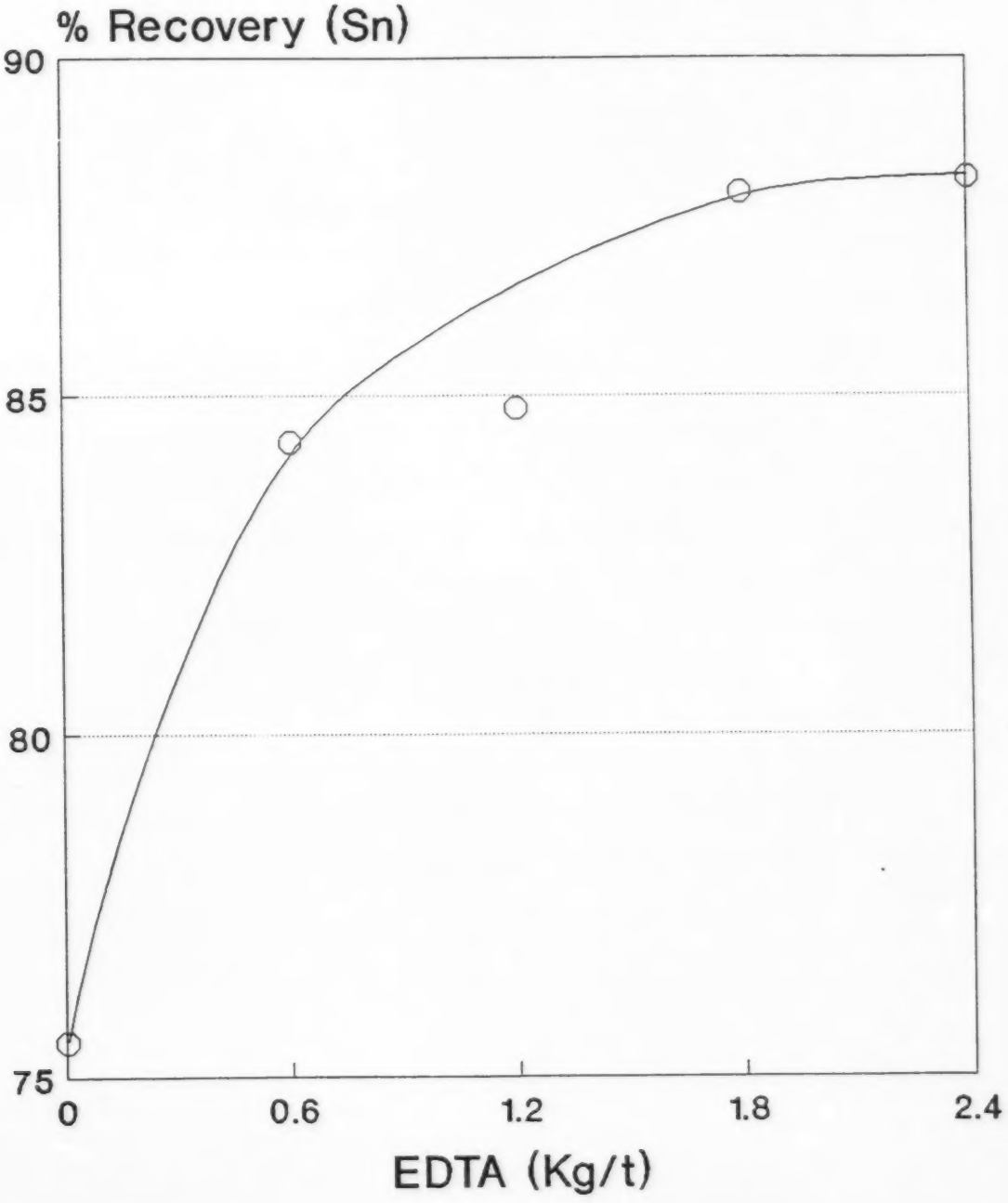
The influence of EDTA on tin recovery is shown in Fig. 3.

The optimum addition of the complexing reagents was: 1.8 kg/t EDTA and 0.5 kg/t $Na_2SiF_6$ in the 1st Rougher Flotation. Another 200 g/t $Na_2SiF_6$ is probably required in the 2nd and 3rd Rougher Flotation.

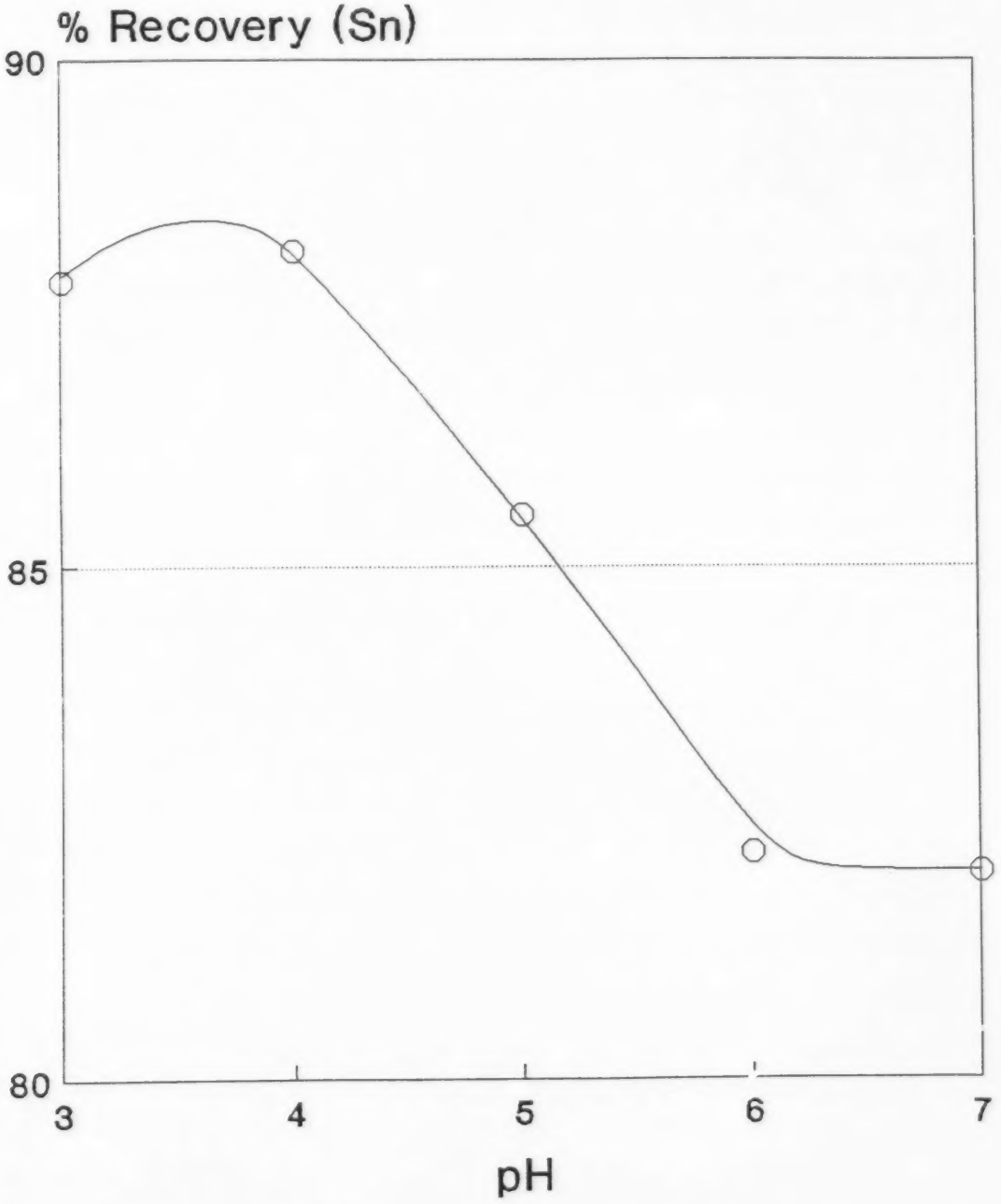
b) pH

In the presence of the complexing agents EDTA and $Na_2SiF_6$ the most favourable conditions for tin flotation were achieved at a pH of 4 (Fig. 4). Sulphuric acid was used as a pH regulator.

Fig. 3 - EDTA Influence on Tin Recovery



# Fig. 4 - pH Influence on Tin Recovery



c) Collector addition

Briquest consumption was studied under optimum conditions of pH and complexing reagents addition. It was found that in open circuit about 600 g/t of the Briquest collector is required in the 1st Rougher Flotation (Fig. 5). Additional amounts of 200 g/t collector was used on each of the 2nd and 3rd Rougher Flotation steps.

d) Frother

The DF-250 was the preferred frother for tin flotation. Its addition was based on the visual observation of the froth. A consumption of 50 g/t in the 1st Rougher and 25 g/t in each of the 2nd and 3rd Rougher Flotation steps was used.

e) Flotation stages and time

To maximize tin recovery it was found necessary to collect two or even three consecutive concentrates. A successive addition of reagents led to better total recovery than a single larger amount supplied at the beginning of the flotation process.

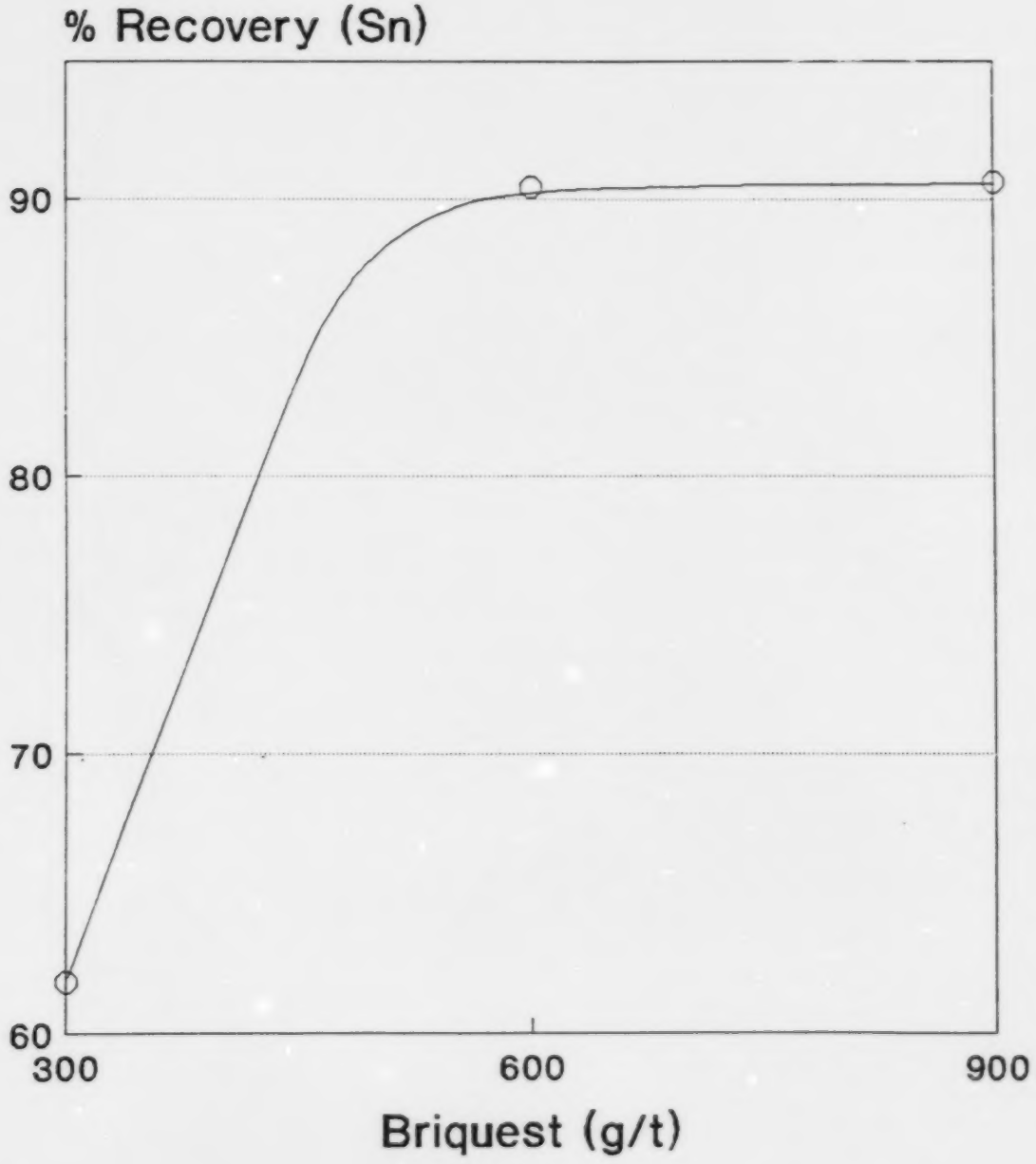
The required flotation time was between 1-2 minutes for each tin concentrate.

f) Upgrading the tin concentrate

The tin rougher concentrate was subjected to successive cleaning stages to obtain a saleable product (over 50% Sn). Five cleaning steps were performed to achieve this target.

However it should be noted that the reagent consumption and the number of cleaning stages represent laboratory open circuit conditions. It is expected that in continuous, closed circuit operation the reagent consumption and the number of cleaning steps could be reduced.

# Fig. 5 - Briquest Influence on Tin Recovery



The conditions and results of the best flotation tests for tin extraction are presented in Tables 7 and 8.

**Table 7. Flotation Conditions**

| Flotation Step | | Reagents | | | pH | Flotation time, min. |
|---|---|---|---|---|---|---|
| | | Type | g/t | Condition min. | | |
| Sulphides Removal | | Na-isoprophylxanthate | 25 | 3 | | |
| | | MIBC* | 50 | 1 | | |
| | | - | - | - | 6.3 | 2 |
| Tin Flotation | Rougher-1 | EDTA** | 1800 | 5 | 4.6 | |
| | | Na-silicofluoride | 500 | 5 | 5.2 | |
| | | Sulphuric acid | 500 | | 4.0 | |
| | | Briquest | 600 | 6 | 4.0 | |
| | | D.F.-250*** | 50 | 1 | | |
| | | - | - | - | 4.0 | 2 |
| | Rougher-2 | Na-silicofluoride | 100 | 3 | 4.4 | |
| | | Sulphuric acid | 130 | | 4.0 | |
| | | Briquest | 200 | 3 | 4.0 | |
| | | DF-250 | 25 | 1 | | |
| | | - | - | - | 4.0 | 1.5 |
| | Rougher-3 | Na-silicofluoride | 100 | 3 | 4.4 | |
| | | Sulphuric acid | 100 | | 4.0 | |
| | | Briquest | 200 | 3 | 4.0 | |
| | | DF-250 | 25 | 1 | | |
| | | - | - | - | 4.0 | 1.5 |
| | 1st Cleaner | EDTA | 67 | 5 | 5.1 | |
| | | Na-silicofluoride | 33 | 5 | 4.6 | |
| | | Briquest | 33 | 5 | 4.8 | |
| | | - | - | 0 | 5.0 | 3 |
| | 2nd Cleaner | Na-silicofluoride | 16 | 3 | 4.3 | |
| | | Briquest | 16 | 3 | 4.5 | |
| | | - | - | - | 4.9 | 2 |
| | 3rd Cleaner | Na-silicofluoride | 16 | 3 | 3.7 | |
| | | Briquest | 16 | 3 | 4.0 | |
| | | - | - | - | 4.9 | 2 |
| | 4th Cleaner | - | - | - | - | |
| | | - | - | - | 5.0 | 1 |

* Methylisobutylcarbinol
** Di-sodium ethylene tetra acetic acid
*** DowFroth-250 frother

**Table 8. Flotation Results**

| Products | % Weight | Assay % | | % Distribution | |
|---|---|---|---|---|---|
| | | S | Sn | S | Sn |
| Pyrite Conc. | 3.7 | 25.6 | 0.64 | 88.0 | 3.1 |
| Tin 4th Cl. Conc. | 1.2 | 0.66 | 54.9 | 0.7 | 85.2 |
| Tin 4th Cl. Tails | 0.3 | 5.03 | 5.90 | 1.4 | 2.3 |
| Tin 3rd Cl. Tails | 0.5 | 2.23 | 1.95 | 1.0 | 1.3 |
| Tin 2nd Cl. Tails | 0.9 | 1.36 | 0.58 | 1.1 | 0.6 |
| Tin 1st Cl. Tails | 3.2 | 0.65 | 0.26 | 1.9 | 1.0 |
| Tin Rougher Tails | 90.2 | 0.07 | 0.056 | 5.9 | 6.5 |
| Head (calc.) | 100.0 | 1.08 | 0.77 | 100.0 | 100.0 |
| Tin 3rd Cl. Conc. | 1.5 | 1.53 | 45.13 | 2.1 | 87.5 |
| Tin 2nd Cl. Conc. | 2.0 | 1.70 | 34.35 | 3.1 | 88.8 |
| Tin 1st Cl. Conc. | 2.9 | 1.59 | 23.86 | 4.2 | 89.4 |
| Tin Rougher Conc. | 6.1 | 1.10 | 11.48 | 6.1 | 90.4 |

The tin final concentrate contained 0.2% As.

## ACKNOWLEDGEMENTS

The author wishes to extend grateful acknowledgement to the Chemical Laboratory, in particular to Mr. Lloyd Dalton for his work to provide a large volume of assays under so many various conditions and with an extremely high degree of accuracy.

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3. J. de Cuyper, "Proprietes electrocinetiques de la cassiterite et de la siderite en relation avec leur flotabilité", The VIII-e Congres International de preparation dis minerais, Leningrad 1968.

4. D.N. Collins, R. Wright and D. Watson, "Use of alkyl imino-bis-methylene phosphonic acids as collectors for oxide and salt-type minerals", Rome, Italy, September 1984.

# APPENDIX 1

# Image analysis of a sample from Eastkemptville (Second Part)

R. Lastra R. Pinard

April 9,1990
Revised April 23, 1990
M-4198 Project: 30.13.07
MSL No. 0083

**Abstract**

A sample of the flotation feed (mainly table tailing) from Eastkemptville was studied by image analysis[1] to determine modal analysis and liberation of the sulphides minerals. The mineral quantities (wt%) in the sample are: quartz 75.8%, mica (illite) and plagioclase (anorthite) 17.0%, apatite 3.1%, pyrite 2.2%, pyrrhotite 0.1%, chalcopyrite and sphalerite 0.4%, arsenopyrite 0.4%, cassiterite 1.0%.

When particles with at least 80% of a given phase are considered as "free"; 90% of the pyrite is "free"; 80% of the chalcopyrite-sphalerite is "free"; and 86% of the arsenopyrite is "free". The small amount of pyrrhotite is essentially locked with pyrite particles.

## 1 Introduction

On January 10, 1990 Mr. Marius Cristovici from MSL/LSM (CANMET) submitted a sample from Eastkemptville. The sample represents the flotation feed and consists mainly of table tailing. The sample assays approximately 0.8wt% Sn.

A report dealing with cassiterite liberation was issued on February 27, 1990. On March 14, 1990, (Lastra et al. 1990). Mr. Cristovici requested additional information on the same sample; namely to identify the presence of sulphides other than pyrite, pyrrhotite, chalcopyrite, and sphalerite and to determine the liberation of the sulphide minerals and their associations.

[1]Keywords: Image Analysis, mineral quantities, size analysis, liberation.

## 2 Method of investigation

The polished section that was used for determination of cassiterite liberation was re-analyzed with the microprobe SEM-IPS image analysis system (MP-SEM-IPS).

## 3 Results

### 3.1 Mineral Quantities

The presence of the major phases and sulphides previously determined was confirmed. Arsenopyrite was more difficult to detect. After searching the entire polished section eight small (2 to 12 $\mu$m) grains and one large (52 $\mu$m) free grain were found. Mineral quantities as reported in Table 1 were determined by the image analysis in vol% and converted to wt% using appropriate specific gravities. The results are comparable with the previous reported modal analysis. It should be noted that due to the characteristics of occurrence of the arsenopyrite, its reported weight percent could be inaccurate; i.e. the solitary and large arsenopyrite grain represents 83% of the arsenopyrite measured.

### 3.2 Liberation

Liberation of cassiterite was reanalized and the results were nearly identical as those previously reported.

The results for liberation of the sulphides are presented in Figures 1 to 6. Figures 1, 3, and 5 plot percent of the sulphide in the sample (PHAREA, y-axis) that is in particles with a given sulphide percent (PHPERC, x-axis). Figures 2, 4, and 6 plot percent of the sulphide (free and lock) in the sample (PHAREA, y-axis) that is in grains of a given size (PHSIZE, [$\mu$m], x-axis).

For pyrite Figure 1 shows that $\approx$90% of the pyrite in the sample is in particles with at least 90% pyrite. Figure 2 indicates the size distribution of the pyrite grains ( $\approx$80% -55 $\mu$m, $K_{80}$ ).

The small amount of pyrrhotite in the sample gives less confidence to the liberation data. An important fraction of the pyrrhotite is locked (Figure 3). The largest bar in Figure 4, represents a locked pyrrhotite grain with a grain size $\approx$17 $\mu$m. This large pyrrhotite grain is associated with pyrite.

Chalcopyrite-sphalerite exhibit (Figure 5) good liberation. Approximately 80% of the chalcopyrite-sphalerite is in particles with at least 80% chalcopyrite-sphalerite. Figure 6 discloses the size distribution of the chalcopyrite-sphalerite grains ( ≈80% -30 $\mu$m).

For arsenopyrite, 86% of it is totally free but 83% is represented by one grain of ≈55 $\mu$m.

# 4 Conclusions

1. The mineral quantities (wt%) in the sample are: quartz 75.8%, mica (illite) and plagioclase (anorthite) 17.0%, apatite 3.1%, pyrite 2.2%, pyrrhotite 0.1%, chalcopyrite and sphalerite 0.4%, arsenopyrite 0.4%, cassiterite 1.0%. The results are comparable with the previous reported modal analysis.
2. When particles with at least 80% of a given phase are considered as "free"; the following proportions of sulphide minerals are "free": 90% of the pyrite; 80% of the chalcopyrite-sphalerite; and 86% of the arsenopyrite. The small amount of pyrrhotite is essentially locked with pyrite particles.
3. The size of the sulphides grains is: for pyrite and arsenopyrite ≈80% -55 $\mu$m, for chalcopyrite- sphalerite ≈80% -30 $\mu$m, and for pyrrhotite ≈80% -17 $\mu$m.

# 5 References

1. R. Lastra, R. Pinard and P. Carrière, 1990, Image Analysis of a sample from East Kemptville. Process Mineralogy, MSL, CANMET, EMR, Section Report M-4183. 5pp.

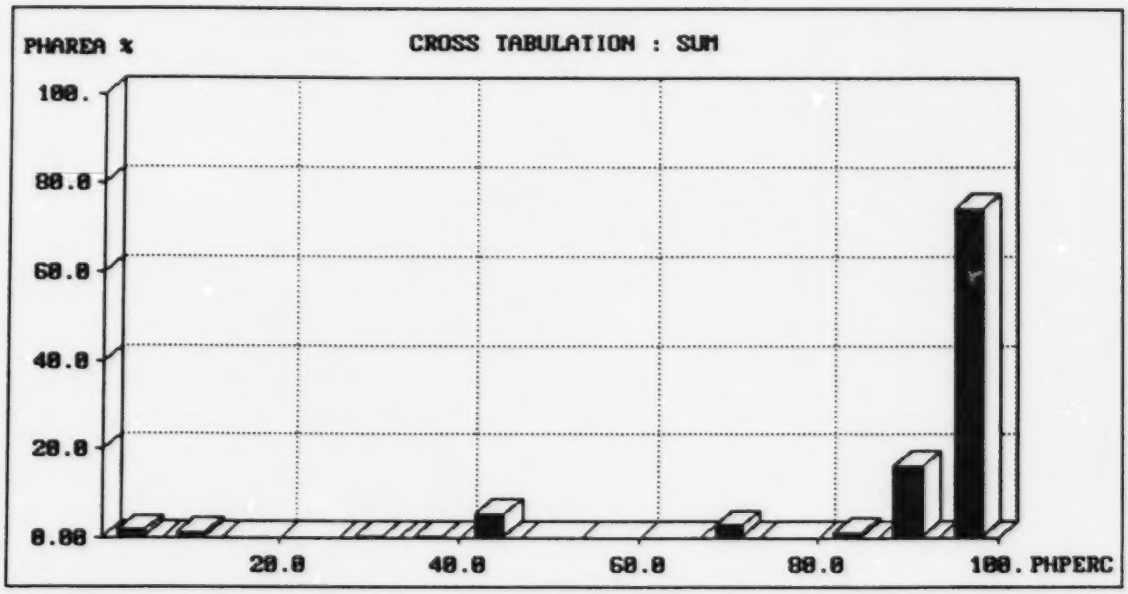


Figure 1: Volumetric percent of the pyrite in the sample (x-axis) that is in particles with a given pyrite percent (x-axis).

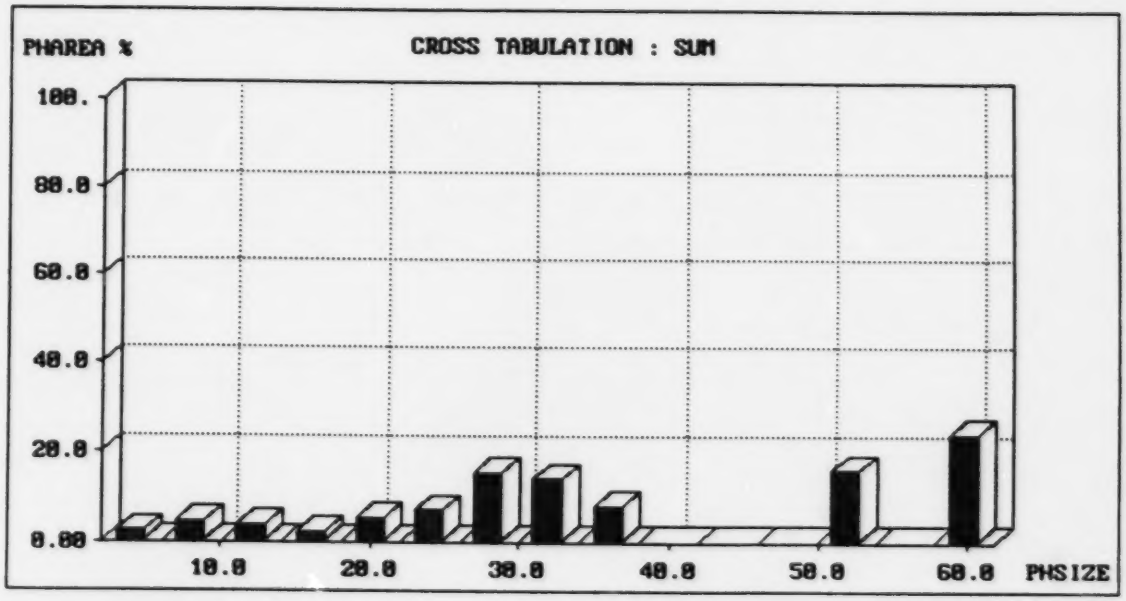


Figure 2: Size distribution of the pyrite grains. Percent of pyrite (PHAREA) present in grains of a given size (PHSIZE, $\mu$m ).

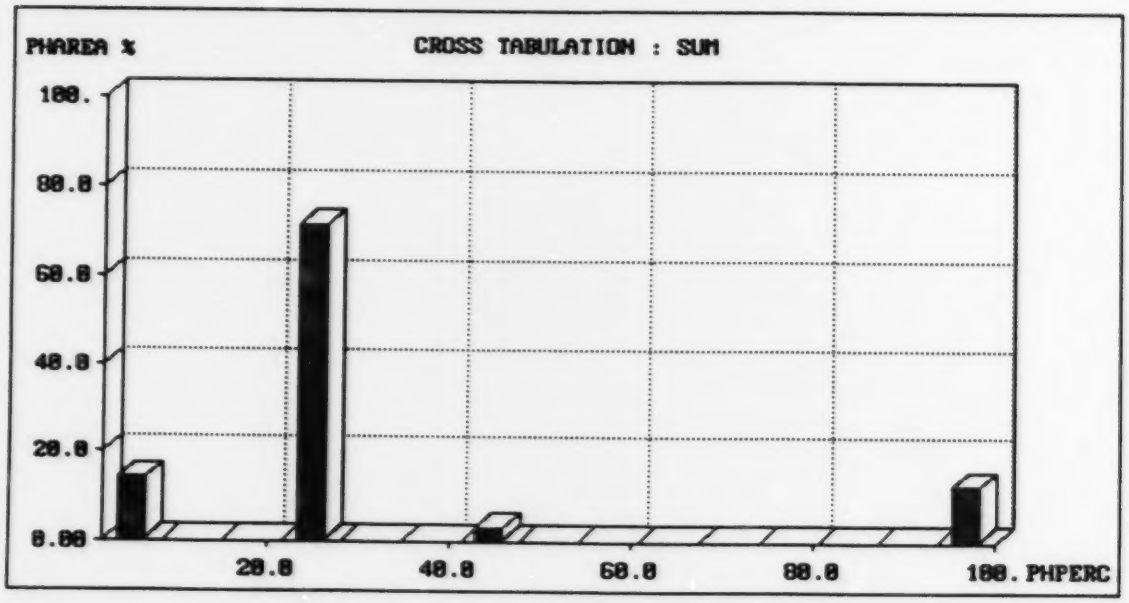


Figure 3: Volumetric percent of the pyrrhotite in the sample (x-axis) that is in particles with a given pyrrhotite percent (x-axis).

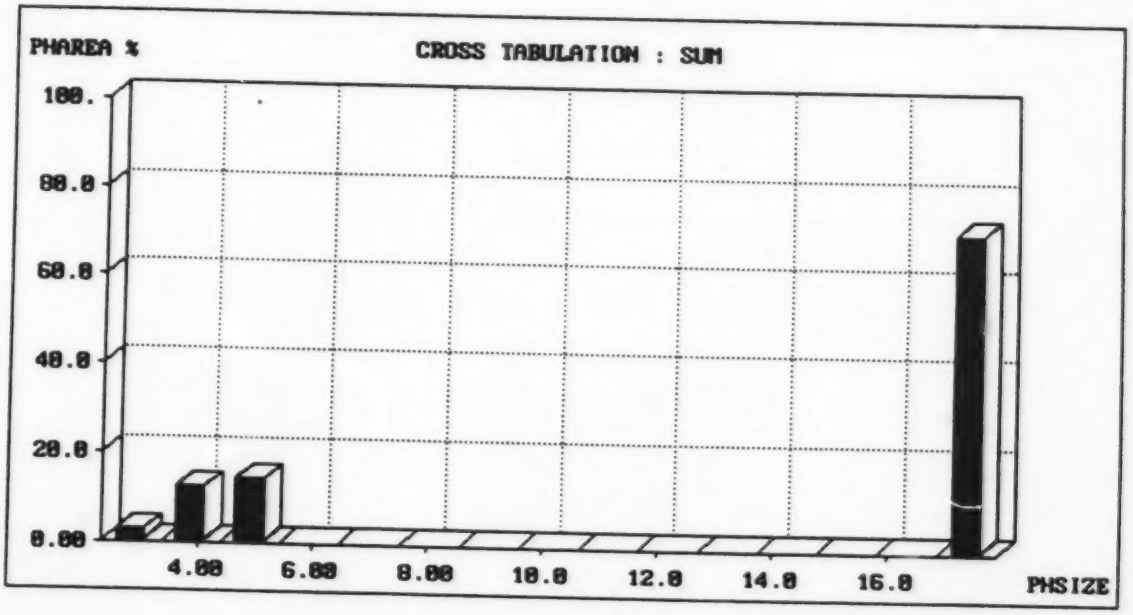


Figure 4: Size distribution of the pyrrhotite grains. Percent of pyrrhotite (PHAREA) present in grains of a given size (PHSIZE, $\mu$m ).

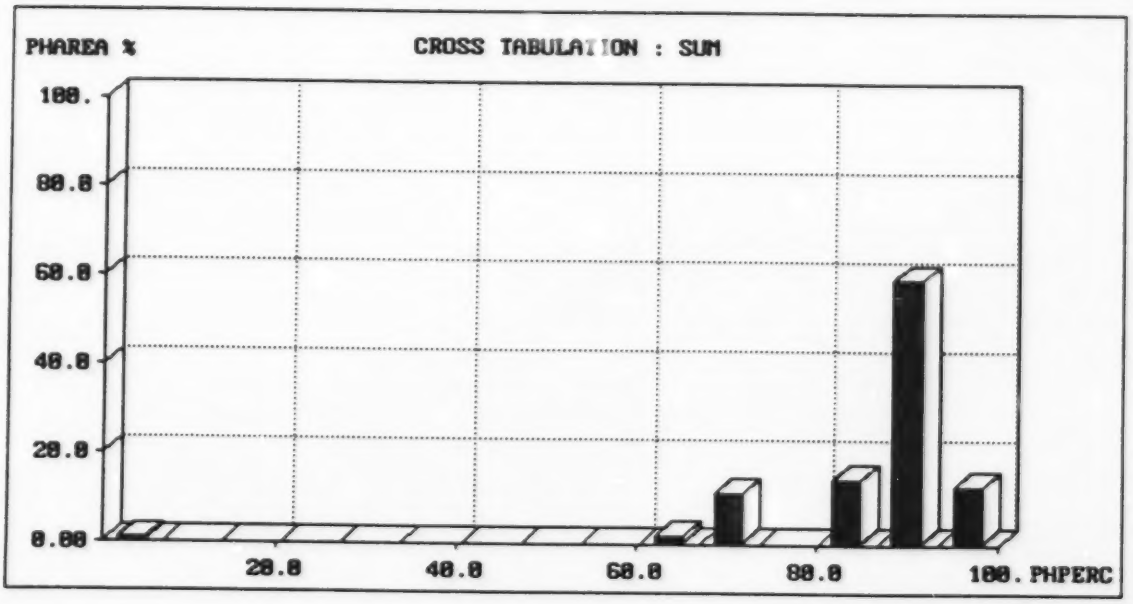


Figure 5: Volumetric percent of the chalcopyrite-sphalerite in the sample (x-axis) that is in particles with a given chalcopyrite-sphalerite percent (x-axis).

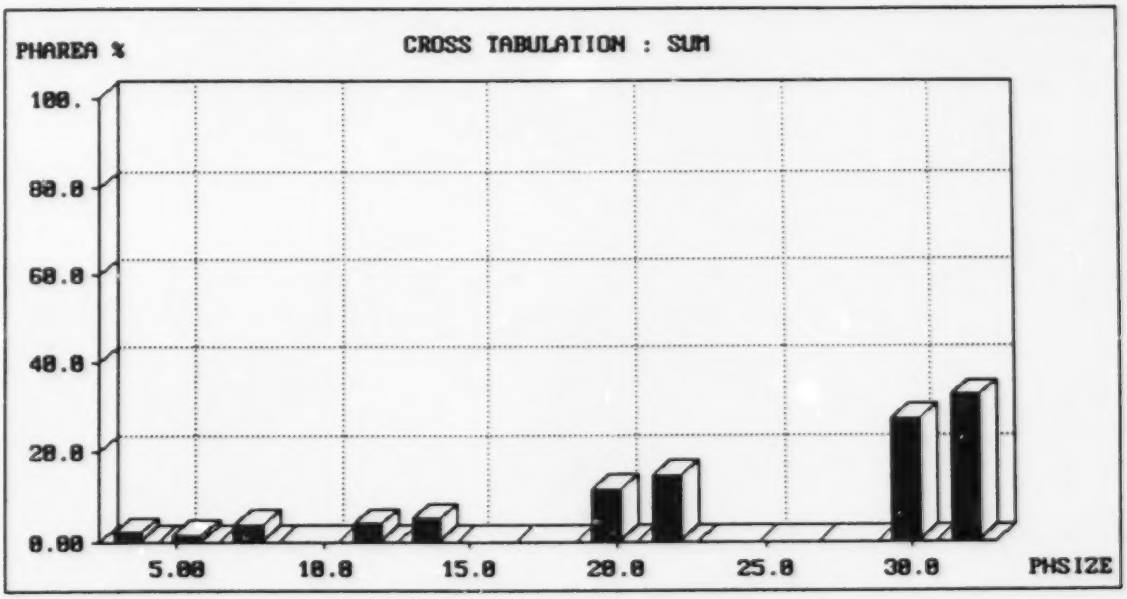


Figure 6: Size distribution of the chalcopyrite-sphalerite grains. Percent of chalcopyrite-sphalerite (PHAREA) present in grains of a given size (PHSIZE, $\mu$m ).

Table 1: Mineral quantities in the flotation feed of Eastkemptville.

| Mineral | WEIGHT % |
|---|---|
| Quartz | 75.8 |
| Mica (illite) and plagioclase (anorthite) | 17.0 |
| Apatite | 3.1 |
| Pyrite | 2.2 |
| Pyrrhotite | 0.1 |
| Chalcopyrite and sphalerite | 0.4 |
| Arsenopyrite | 0.4 |
| Cassiterite | 1.0 |
| Galena | $\approx 0$ |